Nafta-Gaz 2024, no. 2, pp. 102–108, DOI: 10.18668/NG.2024.02.05

The use of new effective compositions for decomposing a stable water-oil emulsion

Zastosowanie nowych skutecznych kompozycji do rozdzielania stabilnej emulsji wodno-ropnej

Guseyn R. Gurbanov[1], Vali Kh. Nurullayev[2], Aysel V.Gasimzade[1]

[1] *Azerbaijan State Oil and Industry University*
[2] *State Oil Company of the Republic of Azerbaijan (SOCAR)*

ABSTRACT: A sample of crude oil from Umbaki oil field, characterized by the property of forming an aggregative and kinetically stable water-oil emulsion has been studied in the work. To conduct the research, Dissolvan-4411, Difrol-9426, Sarol-412, Dissolvan-13280 and ND-12 demulsifiers were examined at concentrations of 200, 400 and 600 g/t and the optimal consumption rate was determined. Laboratory experiments were carried out at temperatures of 20, 40 and 60°C. 10 compositions were prepared with a 1:1 ratio of each reagent, based on the optimal consumption rate of 600 g/t. The compositions are reagents with the same purpose, prepared on the basis of demulsifiers. New compositions of W-series were prepared on the basis of the most preferred compositions of A-series. The efficiency of demulsification was investigated, and, experiments were carried out to measure the quantities of asphaltene, resin and paraffin sediments, as well as the remaining amounts of salts and mechanical mixtures after demulsification of oil. The results of the conducted experimental studies revealed that the effect of compositions is superior to the effect of individual reagents. This is explained by the synergism effect between the reagents. As a result, the impact of compositions on the rheology of stable water-oil emulsions becomes stronger. The amount of chloride salts, mechanical mixtures and asphaltene-resin-paraffin compounds in the oil also decreases sharply. Finally, the dependence of the thickness of the best-performing W series compositions on viscosity, which is an important rheological parameter of oil, is shown in a diagram. The W-2 composition is recommended for wide application in mining conditions as a multifunctional reagent in the oil industry.

Key words: demulsifier, demulsification, water-oil emulsions, composition, crude oil, viscosity, mechanical mixtures, asphaltene, resin, paraffin.

STRESZCZENIE: W pracy wykorzystano próbkę ropy naftowej ze złoża Umbaki, która cechuje się tworzeniem zagregowanej i stabilnej kinetycznie emulsji wodno-ropnej. W celu przeprowadzenia prac badawczych zbadano stężenia deemulgatorów Dissolvan-4411, Difrol-9426, Sarol-412, Dissolvan-13280 i ND-12 w ilościach 200, 400 i 600 g/t oraz określono optymalną wielkość ich zużycia. Doświadczenia laboratoryjne przeprowadzono w temperaturach 20, 40 i 60°C. Przygotowano 10 kompozycji w stosunku 1:1 każdego pojedynczego odczynnika zgodnie z optymalną szybkością zużycia 600 g/t. Kompozycje są odczynnikami o tym samym przeznaczeniu, sporządzonymi na bazie deemulgatorów. Nowe kompozycje serii W przygotowano w oparciu o najbardziej preferowane kompozycje serii A, a po zbadaniu skuteczności deemulgacji przeprowadzono doświadczenia dotyczące ilości osadów asfaltenów, żywic, jak również soli i mieszanin mechanicznych pozostałych po deemulgowaniu ropy. Wyniki przeprowadzonych badań eksperymentalnych wykazały, że efekt zastosowania mieszanin jest lepszy niż efekt oddziaływania pojedynczych odczynników. Można to wytłumaczyć efektem synergii pomiędzy odczynnikami. W rezultacie wpływ kompozycji na reologię stabilnych emulsji wodno-ropnych będzie bardziej znaczący. Gwałtownie zmniejsza się także ilość soli chlorkowych, mieszanin mechanicznych i związków asfaltenowo-żywicowo-parafinowych w ropie. Ponadto na wykresie przedstawiono zależność grubości najlepiej działających kompozycji serii W od lepkości, która jest ważnym parametrem reologicznym ropy. Kompozycja W-2 zalecana jest do szerokiego stosowania w warunkach górniczych jako wielofunkcyjny odczynnik w przemyśle naftowym.

Słowa kluczowe: deemulgator, deemulgacja, emulsje wodno-ropne, skład, ropa naftowa, lepkość, mieszaniny mechaniczne, asfalten, żywica, parafina.

Corresponding author: H.G. Gurbanov, e-mail: *ebikib@mail.ru*

Article contributed to the Editor: 02.10.2023. Approved for publication: 18.01.2024.

Introduction

As it is widely known, the proportion of heavy oil within the annual volume of production in developed oil industry countries is steadily increasing. Given the large number of high-molecular compounds in their compositions, both production and preparation of these oils for transportation poses a number of challenges. Various reagents are employed in the bottom zone of heavy oil fields to facilitate production. While these reagents prove effective during production, they concurrently increase the stability of formation waters and heavy oils. As a result of the influence of all mentioned factors, a solvated layer is formed around the water-dispersed phases inside the produced heavy oils, which prevents the coalescence of the dispersed phases. No matter how intensively the dispersed phases of non-coalescent water collide as a result of Brownian motion, they cannot separate from the oil composition and settle. Consequently, the preparation of such heavy oils for transportation in mining conditions requires high concentration reagent consumption and additional heating (Lutfullin et al., 2005; Nebogina et al., 2008), a practice acknowledged as economically unfavorable. While the temperature alone is sufficient to decompose emulsions produced by light oils, the natural influence of temperature alone is insufficient to decompose emulsions produced by heavy oils in this process. From this point of view, it is more appropriate to use the chemical decomposition method, that is, demulsifiers. As a result of the conducted research, it was determined that the use of demulsifiers individually, as well as their preparation and application in the form of a composition, is more effective in the decomposition of heavy water-oil emulsions. Since most of the oils produced in the world are heavy oils, the use of demulsifiers is currently widespread (Bakhtizin et al., 2016; Gurbanov and Gasimzada, 2022). The demulsifiers used in our research are widely used reagents in the oil industry in both Russia and Azerbaijan. Reagents produced in Russia have been used for some time in Azerbaijan to prepare oils for transportation in mining conditions (Mukhamadiyev and Notov 2008; Gurbanov and Gasimzada, 2023).

As we mentioned above, the majority of produced oils are heavy oils. There are numerous oil fields in Azerbaijan, categorized to the heavy oil group: Muradkhanli, Pirallahi, Umbaki, Bulla-deniz, and others, falling within this oil type (Schubert and Armbruster 1992; Verruto and Kilpatrick, 2008). Those oils differ from other oils due to a high percentage of high-molecular compounds, i.e., resin, asphaltene components, and naphthenic acids, which cause a number of difficulties in the production and transportation of this type of oil (Matiyev et al., 2016; Ali and Alqam, 2000).

Crude oil extracted from Umbaki oil field was used as the research object in the article. The presence of a large amount of resin components in the composition of this oil increases the concentration, leading to its classification to the group of heavy oils (Al-Sahhaf et al., 2008; Pal et al., 2021).

Research objective is to study the protective efficiency of individual reagents and new multifunctional compositions in laboratory conditions.

Research methodology

One of the widely used methods for assessing the demulsification ability of reagents and their compositions is the "Coldfingertest" (static settling) method. In this procedure, reagents or compositions are first dissolved in a solvent and then added in varying concentrations to the packaged oil samples to be investigated. Following the addition of reagents, thorough mixing is conducted for 1 minute, and the mixture is subsequently kept in a water bath. The separation of water is recorded at different intervals based on the demulsification ability of the investigated demulsifier. The demulsification index can be calculated using the following equation:

$$\text{water separation } \% = V/V_o \cdot 100$$

where V represents the volume of water separated after the addition of the demulsifier, and V_o represents the volume of initial water in the crude oil emulsion.

Laboratory tests were modeled in specific technological modes, taking into account separation temperature, dehydration time, hydrodynamic characteristics, dosing, hydration of products. Demulsifiers were dosed in commodity forms, and continuous decomposition of water-oil emulsions was carried out at temperatures of 20, 40, 60°C. The main assessment criteria, considering oil dehydration dynamics, included the residual amount of water in oils, quality of water and the wall of precipitator-cylinders in accordance with GOST-39-133-81.

The reagents used in conducting experiments in laboratory conditions are demulsifiers such as Dissolvan-4411 (Russian production), Dissolvan-13280 (Russian production), Difron-9426 (Russian production), Sarol-412 (Russian production) and ND-12 (Azerbaijani production) and compositions prepared based on them labeled "A"-1, "A"-2, "A"-3, "A"-4, "A"-5, "A"-6, "A"-7, "A"-8, "A"-9 and "A"-10. The content of the "A" based compositions is as follows:

- "A"-1 Dissolvan 4411 + Difron 9426;
- "A"-2 Dissolvan-4411 + Dissolvan-13280;
- "A"-3 Dissolvan-4411 + Sarol-412;
- "A"-4 Dissolvan-4411 + ND-12;
- "A"-5 Difron 9426 + ND-12;
- "A"-6 Difron 9426 + Sarol-412;
- "A"-7 Difron 9426 + Dissolvan-13280;
- "A"-8 Dissolvan-13280 + Sarol-412;

- "A"-9 Dissolvan-13280 + ND-12;
- "A"-10 Sarol-412 + ND-12.

In this research, the demulsification of stable water-oil emulsions extracted from Umbaki field, one of Azerbaijan's heavy oil fields, was conducted using individual and composite reagents at various temperatures and concentrations. The physical and chemical properties of the oil under investigation are presented in Table 1. As shown in this table, the oil selected for this study exhibits a high concentration and belongs to the group of heavy oils. At the same time, the resin content, stemming from high molecular compounds, is quite high. Despite a low quantity of paraffin, the freezing temperature is correspondingly lower than compared to heavy oils.

For comparative analysis, both reagent-based and reagent-free experiments were conducted. In the research on determining the optimal concentration of reagents, tests were conducted at concentrations of 200, 400 and 600, and subsequently the most effective concentration was determined. During the research with the use of 200 g/t reagents, Dissolvan-4411 reagent demonstrated the highest effectiveness, precipitating 54% of the oil with 50% dilution at 60ºC and reducing the residual water in the oil to 23% (Table 2). Following Dissolvan-4411, Difron-9426 yielded favorable result, separating 50% of that dilution from oil and reducing residual water to 25%. ND-12 ranked third in terms of effectiveness, precipitating 48% of water and reducing the water content in oil to 26%. Sarol-412 and Dissolvan-13280 reagents, respectively, separated 44 and 40% of water from oil and increased the amount of dilution to 28 and 30%.

Table 1. Physical and chemical properties of Umbaki crude oil
Tabela 1. Właściwości fizyczne i chemiczne ropy naftowej Umbaki

Parameters	Amount	Method
Density [kg/m^3]	943	ASTM D 4052
Kinematic viscosity [cSt]	360	ASTM D 445
Dynamic viscosity [cP]	339	
Water content [%]	50.00	ASTM D 4007
Mass fraction of mechanical mixtures [%]	2.15	
Freezing temperature [ºC]	–6	ASTM D 97
Mass fraction of paraffin [%]	1.96	UOP 46-64
Mass fraction of resin [%]	17.46	ASTM D 2007
Mass fraction of asphaltene [%]	4.08	IP 143
Chlorine salts content [mg/l]	427.83	GOST-21534-76

The research was continued at concentrations of 400 and 600 g/t and at temperatures of 20, 40, 60°C, and demulsification effects were observed. Dissolvan-4411, Difron-9426 and ND-12 reagents demonstrated the highest effective at both concentrations. In contrast, Sarol-412 and Dissolvan-13280 exhibited lower demulsification effects (Tables 3 and 4).

After the demulsification process of individual reagents, a comparative analysis of the obtained results was carried out by extending the research to include compositions prepared based on those reagents. Each composition was prepared at an optimal concentration of 600 g/t, and the reagents used were added in a ratio of 1:1. From the results of laboratory experiments, it was found that "A"-1, "A"-3, "A"-4 and "A"-5 showed better results than other compositions (Table 5).

A new composition was prepared in a 1:1 ratio from the compositions that showed the best effects, and its efficiency was examined through laboratory experiments (Table 6). The content of new compositions is as follows:

- "A"-1 + "A"-3 = Dissolvan-4411 + Difron-9426 + Sarol-412 = = 2:1:1 (W-1);
- "A"-1 + "A"- 4 = Dissolvan-4411 + Difron-9426 + ND-12 = = 2:1:1 (W-2).

After applying the composition based on each demulsifier to the oil, it induces specific changes in its rheological parameters. Since oil is a colloidal system and the dispersed phases in its composition differ in aggregate state and size, this colloidal property decreases after the application of reagents, which is shown in Table 7. The reagents cause the breakdown of molecular structures consisting of asphaltene, resin and paraffin

Table 2. Results of demulsification of reagent free and reagents at a concentration of 200 g/t
Tabela 2. Wyniki deemulgacji bezodczynnikowej i odczynnikowej w stężeniu 200 g/t

Demulsifier	Concentration [g/t]	Initial watering [%]	Percentage amount of water allocated [%]			Final watering [%]		
			temperature [°C]			temperature [°C]		
			20	40	60	20	40	60
Dissolvan-4411	200	50	25	35	54	37.5	32.5	23
Dissolvan-13280			18	25	40	41.0	37.5	30
Difron-9426			23	32	50	38.5	34.0	25
Sarol-412			20	28	44	40.0	36.0	28
ND-12			22	31	48	39.0	34.5	26
Without reagent	0	50	13	22	30	43.5	38.0	35

deposits (ARPD), which tend to accumulate at the edge of the aqueous phases in the emulsion system.

As a result of numerous experiments, it was found that the demulsification ability of compositions based on individual reagents was higher than individual reagents, and the demulsification ability of new types of compositions based on compositions showed higher results. The effect of W-1 and W-2 compositions on the physical and chemical properties of the oil sample, which was studied by us, was investigated and presented in Tables 8 and 9.

When analyzing the results of laboratory researches of each prepared composition, significant changes are observed in the intensity of change in ARPD, mechanical mixtures, the degree of dilution, and salt content, depending on the composition. These changes have a noticeable impact on the viscosity of the oil sample under investigation, which changes

Table 3. Demulsification results of reagents at a concentration of 400 g/t
Tabela 3. Wyniki deemulgacji odczynników w stężeniu 400 g/t

Demulsifier	Concentration [g/t]	Initial watering [%]	Percentage amount of water allocated [%]			Final watering [%]		
			temperature [°C]			temperature [°C]		
			20	40	60	20	40	60
Dissolvan-4411	400	50	30	44	78	35.0	28.0	11.0
Dissolvan-13280			26	35	60	37.0	32.5	20.0
Difron-9426			28	42	75	36.0	29.0	12.5
Sarol-412			25	37	69	37.5	31.5	15.5
ND-12			29	40	72	35.5	30.0	14.0

Table 4. Demulsification results of reagents at a concentration of 600 g/t
Tabela 4. Wyniki deemulgacji odczynników w stężeniu 600 g/t

Demulsifier	Concentration [g/t]	Initial watering [%]	Percentage amount of water allocated [%]			Final watering [%]		
			temperature [°C]			temperature [°C]		
			20	40	60	20	40	60
Dissolvan-4411	600	50	45	70	92	27,5	15.0	4.0
Dissolvan-13280			36	57	85	32.0	43.0	7.5
Difron-9426			44	68	90	28.0	16.0	5.0
Sarol-412			40	64	86	30.0	18.0	7.0
ND-12			42	65	88	29.0	17.5	6.0

Table 5. Demulsification effect of compositions
Tabela 5. Działanie deemulgujące kompozycji

Demulsifier	Concentration [g/t]	Initial watering [%]	Percentage amount of water allocated [%]			Final watering [%]		
			temperature [°C]			temperature [°C]		
			20	40	60	20	40	60
"A"-1	600	50	50	80	96	25.0	10.0	2.0
"A"-2			42	68	88	29.0	16.0	6.0
"A"-3			45	72	94	27.5	14.0	3.0
"A"-4			46	77	95	27.0	11.5	2.5
"A"-5			48	76	93	26.0	12.0	3.5
"A"-6			44	70	90	28.0	15.0	5.0
"A"-7			41	69	87	29.5	15.5	6.5
"A"-8			40	66	88	30.0	17.0	6.0
"A"-9			43	75	91	28.5	12.5	4.5
"A"-10			47	71	92	26.5	14.5	4.0

Table 6. Demulsification effect of compositions W-1 and W-2
Tabela 6. Działanie deemulgujące kompozycji W-1 i W-2

Demulsifier	Concentration [g/t]	Initial watering [%]	Percentage amount of water allocated [%]			Final watering [%]		
			temperature [°C]			temperature [°C]		
			20	40	60	20	40	60
W-1	600	50	49	81	97	25.5	9.5	1.5
W-2			52	83	98	24.0	8.5	1.0

Table 7. The effect of compositions on the colloidal properties of the oil from the Umbaki field
Tabela 7. Wpływ kompozycji na właściwości koloidalne ropy ze złoża Umbaki

Demulsifier	Concentration	Temperature	ARPD content	Chlorine salts content	Mass fraction of mechanical mixtures
	[g/t]	[°C]	[g/100 g]	[mg/l]	[%]
"A"-1	600	60	15.62	25.96	0.128
"A"-2			19.43	30.64	0.363
"A"-3			16.78	26.17	0.207
"A"-4			16.55	26.06	0.192
"A"-5			16.96	26.21	0.228
"A"-6			17.83	27.55	0.314
"A"-7			19.56	31.72	0.388
"A"-8			19.42	30.31	0.352
"A"-9			17.25	27.42	0.289
"A"-10			17.04	27.08	0.246
W-1			15.39	25.82	0.018
W-2			15.17	23.41	0.011

Table 8. Physical and chemical properties of oil after addition of composition W-1
Tabela 8. Właściwości fizyczne i chemiczne ropy po dodaniu kompozycji W-1

Parameters	Amount	Method
Density [kg/m³]	890	ASTM D 4052
Kinematic viscosity [sSt]	96	ASTM D 445
Dynamic viscosity [sPz]	86	
Water content [%]	1.50	ASTM D 4007
Mass fraction of mechanical mixtures [%]	0.018	
Freezing temperature [°C]	–7	ASTM D 97
Mass fraction of paraffin [%]	1.64	UOP 46-64
Mass fraction of resin [%]	17.67	ASTM D 2007
Mass fraction of asphaltene [%]	3.82	IP 143
Chlorine salts content [mg/l]	25.82	GOST-21534-76

Table 9. Physical and chemical properties of oil after addition of composition W-2
Tabela 9. Właściwości fizyczne i chemiczne ropy po dodaniu kompozycji W-2

Parameters	Amount	Method
Density [kg/m³]	860	ASTM D 4052
Kinematic viscosity [sSt]	94	ASTM D 445
Dynamic viscosity [sPz]	81	
Water content [%]	0.5	ASTM D 4007
Mass fraction of mechanical mixtures [%]	0.011	
Freezing temperature [°C]	–8	ASTM D 97
Mass fraction of paraffin [%]	1.56	UOP 46-64
Mass fraction of resin [%]	16.17	ASTM D 2007
Mass fraction of asphaltene [%]	3.65	IP 143
Chlorine salts content [mg/l]	23.41	GOST-21534-76

proportionally. It is a well-known fact that as oil colloidity increases, its viscosity also tends to be higher. The application of the compositions results in the reduction in the colloidal property, explaining why superior results are obtained at the maximum temperature and optimal concentration of the reagent. According to the research findings, compositions W-1 and W-2 enhance rheological properties of oil more effectively than other compositions.

The relationships between these effects are presented in Figures 1 and 2.

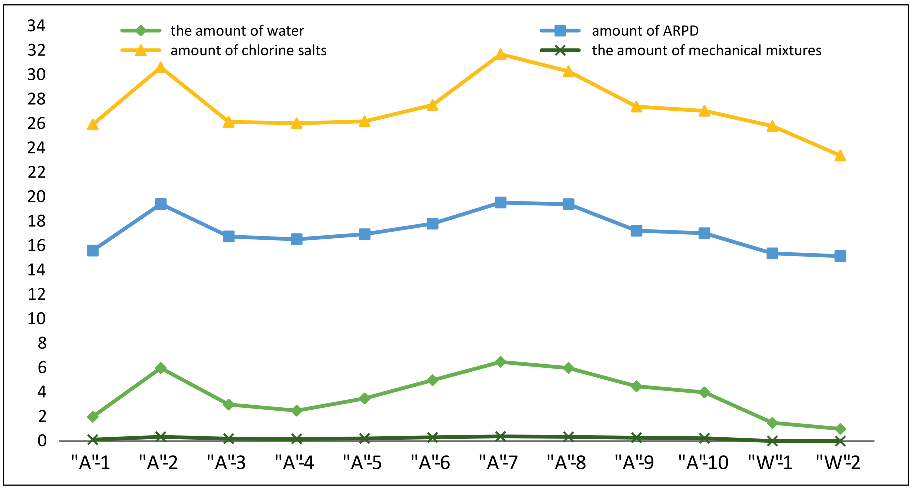


Figure 1. Hydration degree of compositions at 60°C and a concentration of 600 g/t dependence on the amount of ARPD salts and mechanical mixtures

Rysunek 1. Stopień uwodnienia kompozycji w temperaturze 60°C i stężeniu 600 g/t w zależności od ilości ARPD soli i mieszanin mechanicznych

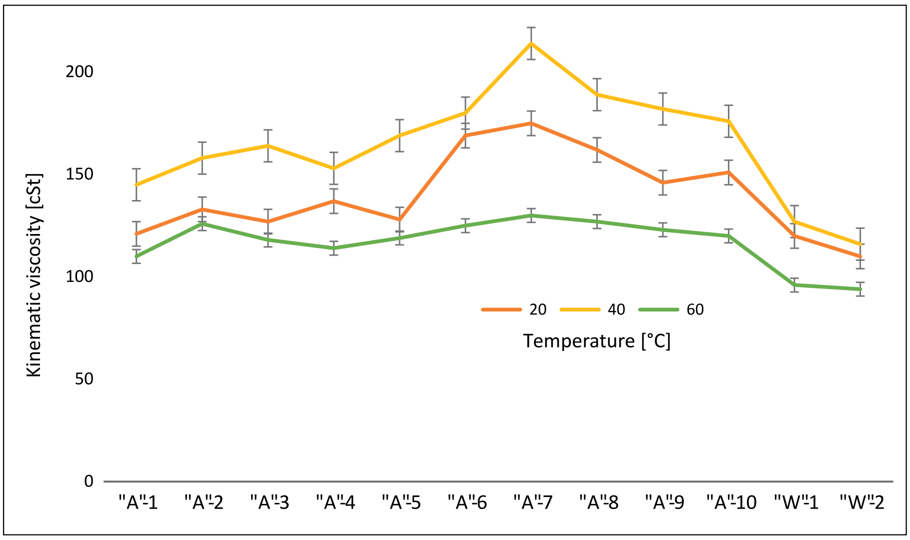


Figure 2. Dependences of compositions on viscosity

Rysunek 2. Zależność składu od lepkości

Conclusions

1. For the first time, the effect of five individual demulsifiers and ten new A-series compositions prepared in different mole ratios on the demulsification of the Umbaki oil sample with a dilution rate of 50% was studied in laboratory conditions. The demulsification process was carried out at temperatures of 20, 40, 60°C and using concentrations of reagents of 200, 400, 600 g/t.
2. Dissolvan-4411 demonstrated the most effective performance among the individual demulsifiers, resulting in a residual dilution of 4% in the Umbaki oil sample at a concentration of 600 g/t at 60°C. Among the A-series compositions, A-1 exhibited the best result at a concentration of 600 g/t and temperature of 60°C, with a residual dilution of 2%.
3. In the demulsification of the Umbaki oil sample at a temperature of 60°C, the more complex W-1 and W-2 compositions based on A-1, A-2, A-3 and A-4 compositions, the residual dilution was 1.5 and 1.0% respectively.
4. When studying the impact of A and W-series compositions on the amount of paraffin deposits, chloride salts, and mechanical mixtures in the oil sample, A-1 and W-2 showed the highest effectiveness.

References

Ali M.F., Alqam M.H., 2000. The role of asphaltenes resins and other solids in the stabilization of water in oil emulsions and its effects on oil production in Saudi oil fields. *Fuel*. 79(11): 1309–1316. DOI: 10.1016/S0016-2361(99)00268-9.

Al-Sahhaf T., Elsharkawy A., Fahim M., 2008. Stability of water-in-crude oil emulsions: effect of oil aromaticity, resins to asphaltene ratio, and pH of water. *Petroleum Science and Technology*, 26(17): 2009–2022. DOI: 10.1080/10916460701428904.

Bakhtizin R.N., Karimov R.M., Mastobayev B.N., 2016. Impact of macromolecular components on rheological properties depending on the structural-group and fractional composition of oil. *SOCAR Proceedings*. 1: 42–50.

Gurbanov H.R., Gasimzada A.V., 2022. Research of the impact of new compositions on the decomposition of stable water-oil emulsions of heavy oils. *Issues of Chemistry and Chemical Technology*, 6: 19–28.

Gurbanov H.R., Gasimzada A.V., 2023. Study on efficiency of new multifunctional compositions for preparation of oil for transportation. *Issues of Chemistry and Chemical Technology*, 4: 41–50.

Lutfullin M.F., Mukhamadiev A.A., Agniev S.V., 2005. Results of application of the demulsifier DecleaveS-1251 in Maloichskoye field of OAO Severnoyeneftegaz TNK-BP. *Journal of Oil Industry*. 5: 94–96.

Matiyev K.I., Aga-zada A.R., Keldibayeva S.S., 2016. Removal of asphalt-resin and paraffin deposits from various fields. *SOCAR Proceedings*, 4: 64–68.

Mukhamadiyev A.A., Notov S.V., 2008. The results of pilot tests of demulsifier "Alkioks-516" by the facilities of OJSC "Samotlorneftegaz". *Journal of Oil Industry*, 5: 74–75.

Nebogina N.A., Prozorova I.V., Yudina N.V., 2008. Impact of water content in oil on the formation and rheological properties of oil-water emulsions. *Journal of Oil Industry*, 12: 90–92.

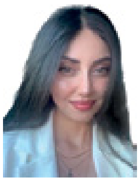
Pal B., Kumar R., Kumar T.N., 2021. Demulsification of crude oil-water emulsion using naturally formulated demulsifier. *Petroleum Science and Technology*, 39: 1027–1042

Schubert H., Armbruster H., 1992. Principles of formation and stability of emulsions. *International Chemical Engineering*, 32: 14–28.

Verruto V.J., Kilpatrick P.K., 2008. Water-in-model oil emulsions studied by small angle neutron scattering: interfacial film thickness and composition. *Langmuir*, 24(22): 12807–12822. DOI: 10.1021/la802095m.

Prof. Guseyn Ramazan GURBANOV, Ph.D.
Head of the Department of Oil and Gas Transportation and Storage
Azerbaijan State Oil and Industry University
16/21 Azadliq Ave., Baku AZ1010, Azerbaijan
E-mail: *huseyn.gurbanov@asoiu.edu.az*

Vali Khanaly NURULLAYEV, Sc.D.
Senior engineer at the Department of Oil Belts, State Oil Company of the Republic of Azerbaijan (SOCAR)
E-mail: *veliehet1973@mail.ru*



Aysel Valiyaddin GASIMZADE, Ph.D.
Assistant Professor at the Department of Oil and Gas Transportation and Storage
Azerbaijan State Oil and İndustry University
Khagani Street 31, Baku AZ1010, Azerbaijan
E-mail: *qasimzade92@inbox.ru*